

PATENT SPECIFICATION

(11) 1337990

1337990

NO DRAWINGS

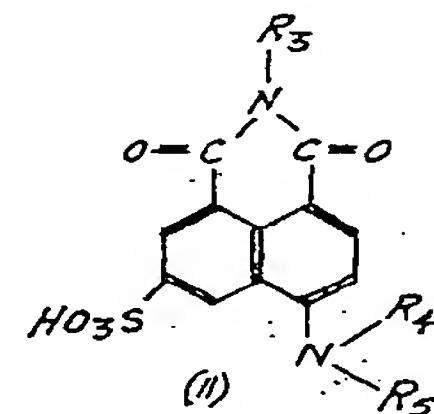
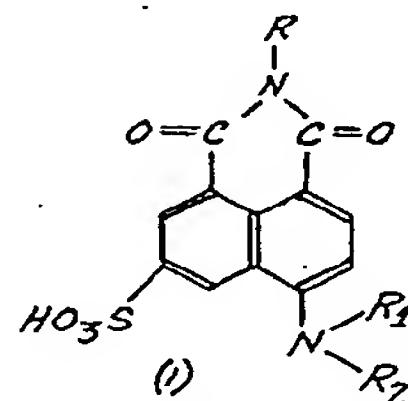
(21) Application No. 59526/70 (22) Filed 15 Dec. 1970
 (31) Convention Application No. 19236 (32) Filed 24 Dec. 1969 in
 (33) Switzerland (CH)
 (44) Complete Specification published 21 Nov. 1973
 (51) International Classification C09B 57/00, 62/20; D06P 3/24, 3/32,
 3/14, 3/60
 (52) Index at acceptance
 C4P D1M
 D1B 2F 2L2 2L5D 2M
 (72) Inventor WERNER KOCH



(54) NAPHTHALIMIDE COMPOUNDS, THEIR PREPARATION AND USE

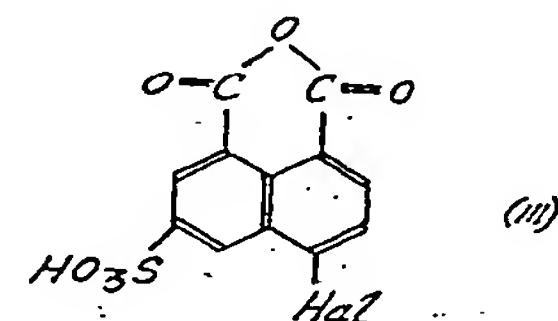
(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle/Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of dyeing material comprising synthetic polyamide, natural or regenerated cellulose fibres, paper, leather, skins, animal hair or a synthetic plastics composition, which comprises applying to said material one or more compounds of the formula

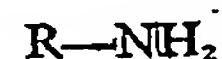


wherein R₃ and R₄, independently each represents an optionally substituted alkyl, aralkyl or cycloalkyl radical, and R₅ represents hydrogen or an optionally substituted alkyl, aralkyl or cycloalkyl radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R₄ and R₅, together with the N-atom to which they are attached, together with a heterocyclic ring. The compounds of formula (I) absorb in the yellow to orange wave range and fluoresce in the green to red wave range:

The compounds of formula (I) can be obtained by reacting 1 mol of a compound of the formula



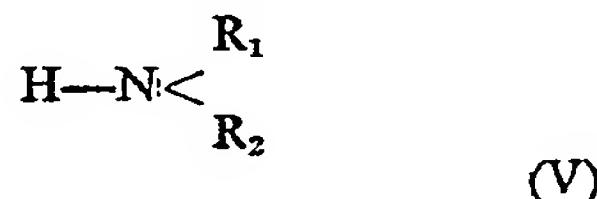
wherein Hal represents a halogen atom, more especially a bromine atom, with one mol of an amine of the formula



(IV)

wherein R and R₁, independently, each represents an optionally substituted hydrocarbon or heterocyclic radical, and R₂ represents hydrogen or an optionally substituted hydrocarbon or heterocyclic radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, that is to say a group containing a substituent which can be split off as an anion and/or a carbon to carbon double or triple bond capable of addition, or R₁ and R₂, together with the N-atom to which they are attached, together form a heterocyclic ring, or salts thereof. In this process it is preferred to use one or more compounds of the formula

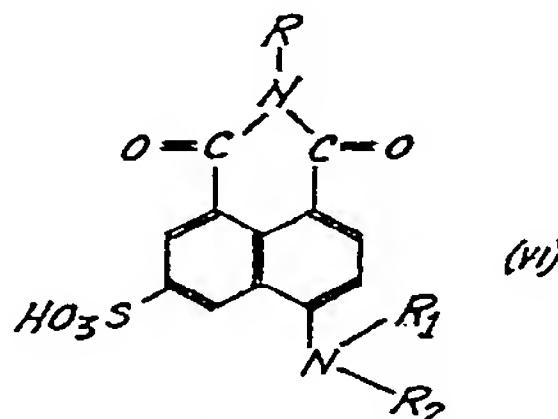
and 1 mole of an amine of the formula



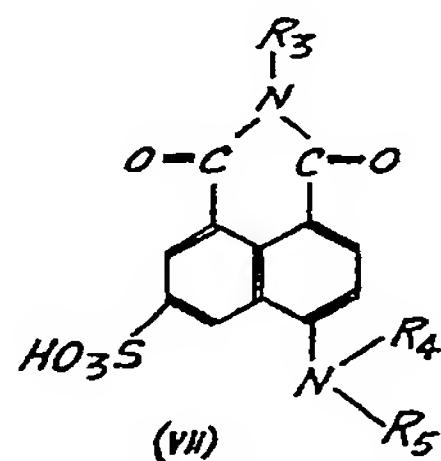
5 Alternatively when R_2 represents a reactive group of the afore-mentioned kind, 1 mol of a compound of formula (III) can be reacted with 1 mol of an amine of the formula (IV) and 1 mole of an amine of the formula R_1-NH_2 , followed by introduction of the reactive group R_2 .

10 A preferred process comprises reacting 1 mol of a compound of formula (III) with 1 mol of a compound of formula (V) and thereafter with 1 mol of a compound of formula (IV).

15 The invention also relates to compounds of the formula



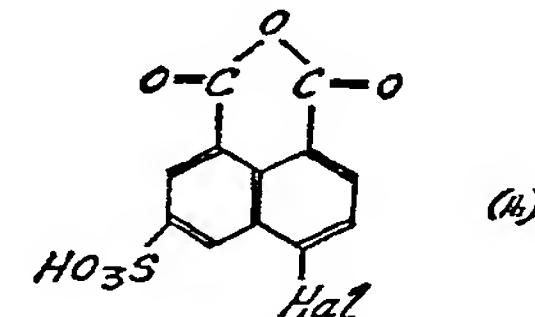
20 wherein R and R_1 , independently, each represents an optionally substituted hydrocarbon or heterocyclic radical, R_2 represents hydrogen or an optionally substituted hydrocarbon or heterocyclic radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R_1 and R_2 , together with the N-atom to which they are attached, together form a heterocyclic ring, with the proviso that, when R_2 represents hydrogen, R and R_1 do not simultaneously represent an unsubstituted alkyl or aralkyl radical. Particularly preferred compounds are those of the formula



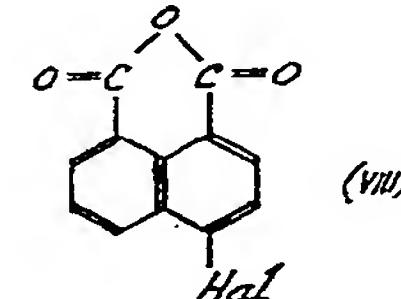
35 wherein R_3 and R_4 , independently, each represents an optionally substituted alkyl, aralkyl or cycloalkyl radical, and R_5 represents hydrogen or an optionally substituted alkyl, aralkyl or cycloalkyl radical or a reactive group cap-

able of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R_1 and R_5 , together with the N-atom to which they are attached, together form a heterocyclic ring, with the proviso that, when R_5 represents hydrogen, R_3 and R_4 do not simultaneously represent an unsubstituted alkyl or aralkyl radical. The invention also relates to a dyeing process for dyeing material comprising natural polyamide fibres which comprises applying to the material one or more compounds of formula (VI).

Compounds of the formula



wherein Hal represents a halogen atom, more especially a bromine atom, can be prepared by sulphonating a compound of the formula



by methods as known *per se*.

Compounds of the formula (VIII) are known.

By way of example, the corresponding bromine derivative is described by P. R. Constantine *et al*, in J.O.C. 34, 1113 (1969) or C Graebe in "Annalen der Chemie" 327, page 85 (1903).

The compounds of formula (I) can be converted into dyeing preparations. The processing, for example, into stable, liquid or solid dyeing preparations can be effected by a generally known method, for example, by grinding or granulating or atomising, or then by dissolving in suitable solvents, possibly with addition of an auxiliary agent, for example, a stabiliser.

Halogen can represent fluorine or iodine but preferably represents chlorine or bromine.

Hydrocarbon radicals are for example optionally substituted alkyl, aralkyl, cycloalkyl or aryl radicals, for example, cyclohexyl, alkylcyclohexyl, halocyclohexyl, phenyl or naphthyl radicals.

Alkyl radicals are, for example, straight-chain or branched alkyl radicals, can contain 1 to 18, or 1 to 12 and usually 1 to 6, but preferably 1, 2, 3 or 4 carbon atoms. If these radicals are substituted, they can contain one

or more substituents selected from halogen atoms, hydroxyl, cyano, sulphonic acid, alkoxy, acyl, amide and amino radicals. Aralkyl radicals include, for example, phenyl-alkyl radicals, a typical aralkyl radical being, for example, a benzyl radical. Alkoxy radicals contain for example 1 to 6 and preferably 1, 2, 3 or 4 carbon atoms.

R₁ and R₂ or R₄ and R₅, together with the N-atom to which they are attached, together can form a saturated or partially saturated, preferably 5-membered or 6-membered heterocyclic compound, for example, a pyrrolidine, piperidine, morpholine, aziridine or piperazine ring.

When R, R₁ or R₂ represents a heterocyclic radical it may be the radical of an optionally substituted saturated, partially saturated or unsaturated multi-membered ring, advantageously a 5-membered or 6-membered ring, on which possibly one or more further cycloaliphatic, heterocyclic or aromatic rings can be condensed. Examples of such heterocyclic radicals are the radicals of pyridine, quinoline, piperidine, pyrrolidine, morpholine, aziridine, piperazine, isoquinoline, tetrahydroquinoline, pyrazole, triazole, pyridazine, imidazole, triazine, pyrimidine, thiazole, benzothiazole, thiadiazole, indazole, imidazole, pyrrole, indole, oxazole, isoxazole, tetrazole, furan, dioxane and thiophene.

All radicals of aromatic character, for example, aromatic-carbocyclic or aromatic-heterocyclic radicals, such as phenyl, naphthyl, tetrahydronaphthyl, pyridyl, quinolyl or tetrahydroquinolyl radicals, can carry one or more substituents selected from for example, halogen atoms, sulphonic acid, carboxylic acid, nitro, amino, cyano, thiocyanato, hydroxyl, alkyl, alkoxy, trifluoroalkyl, trichloroalkyl, phenyl, phenoxy, diphenyloxy, phenylthio, diphenylthio, alkylamino, dialkylamino, acyl, acyloxy, acylamino, such as urethane, acetyl, acetylamino, benzoylamino, alkyl-sulphonyl, aryl-sulphonyl, sulphonic acid amide, sulphonic acid alkylamide, sulphonic acid dialkylamide, sulphonic acid aryl amide group, and arylazo, such as phenylazo, diphenylazo or naphthylazo.

R₂ or R₅ may stand for a reactive group containing a substituent which can be split off to give an anion, for example, the radical derived by removing a halogen atom from a dihalo- or trihalo-1,3,5-triazine, or a di-, tri- or tetra-halo-pyrimidine or an alkylsulphonyl halopyrimidine. R₂ or R₅ may also stand for an acyl radical which carries a substituent which can be split off as anion and/or a carbon to carbon double or triple bond capable of addition. Such groups are for example described in British Patent Specifications 1,144,477 and 1,145,385.

Suitable reactive groups are for example chloroacetyl, β -chloropropionyl, α -chloroacryloyl, 2,3-dichloroquinoxalyl-6-carbonyl, β -(4,5-dichloropyridazonyl-1)-propionyl, 4,6-dichloro-1,3,5-triazinyl-2; 2,6-dichloropyrimidyl-4; 2,5,6-trichloropyrimidyl-4; 4-chloro-6-amino-1,3,5-triazinyl-2; 4-chloro-6-(4'-sulphophenylamino)-1,3,5-triazinyl-2; 5-chloro-2,6-difluoropyrimidyl-4; and β -sulphato-ethylsulphonyl.

The preparation of a compound of formula (I) can take place in water or in an organic solvent, e.g. dioxane, or in a mixture of water and an organic solvent, at a temperature from 70 to 180°C, preferably at 80 to 120°C. If necessary, it is also possible to work under pressure or to carry out the reaction in the presence of a catalyst, such as metallic copper or a copper halide.

The materials referred to can be dyed by generally known methods. The fibres referred to can be dyed, for example, in aqueous alkali or acid medium, or advantageously neutral medium, at temperatures from 60 to 100°C, or at temperatures above 100°C under pressure, or from dispersions, for example, aqueous or organic dispersions. The compounds can be applied from a long dye-bath; however, they can also be applied from a padding or printing. Usually yellow to orange dyeing effects are obtained, the fluorescence emission being at wavelengths λ 500 to 600 μm . The dyeing results on such fibres have good general fastness properties, for example, good wet-fastness properties; they also show good fastness to perspiration, water, sea-water, acid, alkali and milling. The dyeing effects are level and resistant to rubbing. In addition, the compounds of formula (I) cover nylons which dye streakily. They have a good synthesis power, show good migrating properties and have a good resistance to formaldehyde; moreover, they are pH-stable, have good solubility in water and the dyeing can be effected from neutral dye-baths or neutral dispersions. The compounds of formula (I) are also suitable, for example, in the form of their salts, for example alkali metal salts, such as sodium or potassium salts, amine salts or ammonium salts, for the spin-dyeing of synthetic plastics compositions dissolved in organic solvents and of synthetic plastics and lacquers, for example, nitro lacquers or vinyl lacquers, in which they have good fastness to fats and top finishes. Most of the salts are highly soluble in polar organic solvents, such as alcohols, ketones, amines, acetic acid alkyl esters and ethers, (e.g. ethyl alcohol, butyl alcohol, acetone, cyclohexylamine, ethylacetate, amyl acetate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diacetone-alcohol and isophorone).

By synthetic plastics compositions are to be understood solvent-free or solvent-containing compositions consisting of synthetic plastics or synthetic resins.

In the following Examples, the parts represent parts by weight, the percentages represent percentages by weight and the temperatures are in degrees centigrade.

5

Example 1.

10 parts of 4-bromo-1,8-naphthoic acid anhydride are introduced at 20° into a solution prepared from 8.35 parts of sulphuric acid monohydrate and 12.5 parts of 65% oleum.

10

The reaction mass is heated to 50° and stirred for 10 to 20 hours until a sample applied to ice is water-soluble. The preparation, worked up by known methods, is the compound of formula (II) where Hal is bromine. The compound is colourless and has a melting point higher than 300°: it is suitable for the production of dyestuffs, more especially of compounds of formula (I).

15

20

5 parts of 4-bromo-6-sulphon-1,8-naphthalic acid anhydride, dissolved in 25 parts of 50% aqueous dioxane, are refluxed for 10 hours with 4.5 parts of 3,3,5-trimethylcyclohexylamine, with addition of 0.1 part of a catalyst mixture consisting of copper-bronze

25

and cuprous chloride. The reaction mixture is separated from the insoluble substance and the filtrate is concentrated by evaporation. The yield of pure dyestuff which is difficultly soluble in water is 5.4 parts, or 70% of the theoretical.

30

5 parts of the dyestuff are formed into a paste with 4.6 parts of sodium dinaphthylmethane disulphonate and 15 parts of water and dispersed by the usual methods. On polyamide-66 woven fabric, the dyestuff gives yellowish-green fluorescing dyeing effects with good general fastness properties.

Example 2.

35

25 parts of 4-chloro-6-sulpho-1,8-naphthalic acid anhydride, are introduced at 40 lar manner to 4-bromo-6-sulpho-1,8-naphthalic acid anhydride, are introduced at room temperature into 130 parts of cyclohexylamine. The reaction mixture is gradually

45

heated to 100° and kept for 6 hours at this temperature. After cooling, it is poured while continuing cooling on to 173 parts of hydrochloric acid. The precipitated dyestuff is filtered, washed with water and dried at 100°.

50

The water-soluble, neutrally-taking dyestuff provides on polyamide-66 woven fabrics yellowish-green dyeing effects with very good general fastness properties.

Example 3.

55

25 parts of 4-chloro-6-sulpho-1,8-naphthalic acid anhydride are treated in an autoclave at 100° for 10 hours with 150 parts of methylamine. After cooling, the substance

is poured on to hydrochloric acid. The dyestuff which is salted out is washed with brine and dried. It dyes synthetic polyamide in yellowish-green tints with good general fastness properties.

60

Example 4.

30 parts of the dyestuff of Example 3 are dissolved in 500 parts of water and treated at a pH value of 4 to 4.5 with 20 parts of tetrachloropyrimidine for 8 hours at 50°. By adding sodium carbonate, the pH value is kept constant at 4.5. After cooling, the dyestuff can be salted out by adding sodium chloride. After effecting clarification, this dyestuff can be directly used. The reactive dyestuff provides alkali-dyed, beautiful, brilliant, yellow dyeing effects with good general fastness properties on cotton.

65

70

75

Example 5.

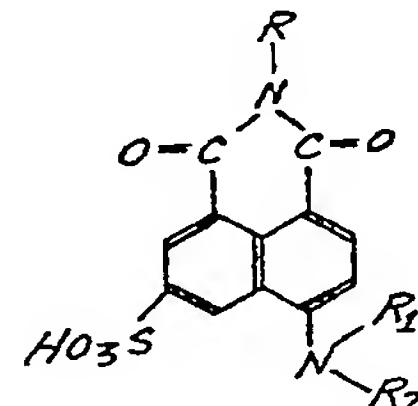
7 parts of 4-bromo-6-sulpho-1,8-naphthalic acid anhydride and 2.7 parts of isopropylamine are refluxed in the presence of 0.5 part of lithium carbonate and 0.1 part of each of cuprous bromide and copper in 50 parts of dimethyl formamide. After 6 hours, the solution is adjusted to be acid and the dyestuff is isolated by usual methods. It can be used as such. If the dyestuff isolated in this way is adjusted to be alkali and heated for 1 to 2 hours under reflux, partial saponification occurs. The regenerated amine can be separated from the sodium salt of the dicarboxylic acid by extraction by shaking from carbon tetrachloride. The aqueous solution of the intermediate product is made acid, 3.4 parts of trimethylcyclohexylamine are added thereto and it is treated under reflux to complete conversion. The dyestuff is isolated by the usual methods. It dyes polyamide-66 woven fabrics in bright yellow tones.

80

The following Table indicates the structural formation of other dyestuffs, such as can be obtained in accordance with the data given in the examples.

85

The symbols R, R₁ and R₂ in the formula



have the meanings indicated in the Table.

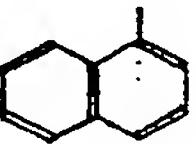
90

95

100

105

Ex. No.	R	R ₁	R ₂	Shade of the dyeing on nylon
6	—CH(CH ₃) ₂	—CH(CH ₃) ₂	H	green-tinged yellow
7			H	do.
8	—C ₂ H ₄ —OH	—C ₂ H ₄ —OH	H	do.
9		—C ₂ H ₄ —OH	H	do.
10		—C ₂ H ₄ —SO ₃ H	H	do.
11	—C ₂ H ₄ —OH	—C ₂ H ₄ —OH	—C ₂ H ₄ —OH	do.
12	—CH—(CH ₃) ₂		H	red-tinged yellow
13		—CH ₃	—CH ₃	green-tinged yellow
14		—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ — R ₁ and R ₂ together		do.
15		—CH—(CH ₃) ₂	H	do.

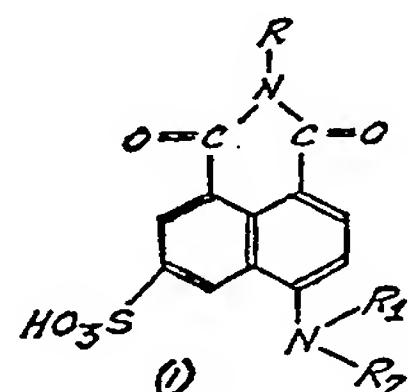
Ex. No.	R	R ₁	R ₂	Shade of the dyeing on nylon
16		—CH—(CH ₃) ₂	H	do.
17	—n—C ₅ H ₁₁	—n—C ₅ H ₁₁	H	do.
18	—C ₅ H ₁₁ (iso)	—C ₅ H ₁₁ (iso)	H	do.
19	—n—C ₄ H ₉	—n—C ₄ H ₉	H	do.
20	—C ₄ H ₉ (iso)	—C ₄ H ₉ (iso)	H	do.

Dyeing Example.

100 parts of pre-moistened nylon cloth are introduced at 40° into a dyebath consisting of 4000 parts of water, 10 parts of anhydrous sodium sulphate and 2 parts of the dyestuff of Example 1. The dye liquor is heated over a period of 30 minutes to boiling temperature, is kept at this temperature for 1 hour, 35
 5 whereupon 4 parts of glacial acetic acid are added and the dyeing is completed by heating to boiling temperature over a period of another 30 minutes. During the dyeing operation, the evaporated water is constantly replaced. Thereafter, the nylon cloth, dyed with a yellowish-green fluorescing shade, is removed from the liquor, rinsed with water and dried. It is also possible to dye wool by the same process. The dyeing effects have good 40
 10 light-fastness and good fastness properties to wet processing.

WHAT WE CLAIM IS:—

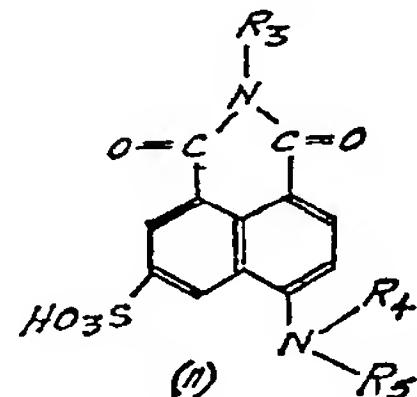
1. A method of dyeing material comprising synthetic polyamide, natural or regenerated cellulose fibres, paper, leather, skin, animal hair, or a synthetic plastics composition, which comprises applying to said material one or more compounds of the formula 45
 25



30 wherein R and R₁, independently, each represents an optionally substituted hydrocarbon or heterocyclic radical, R₂ represents hydrogen

or an optionally substituted hydrocarbon or heterocyclic radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R₁ and R₂, together with the N-atom to which they are attached, together form a heterocyclic ring, or salts thereof.

35 2. A process according to claim 1 wherein there is used one or more compounds of the formula

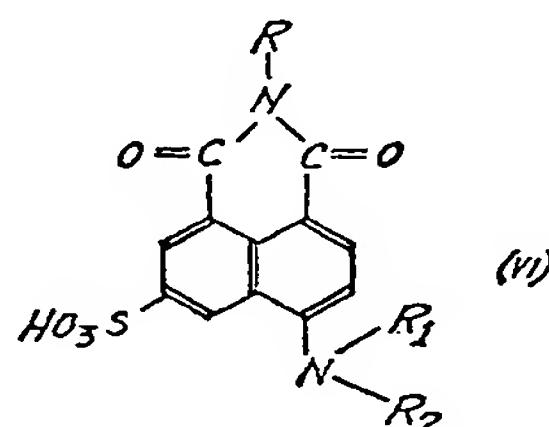


45 wherein R₃ and R₄, independently each represents an optionally substituted alkyl, aralkyl or cycloalkyl radical, and R₅ represents hydrogen or an optionally substituted alkyl, aralkyl or cycloalkyl radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R₄ and R₅, together with the N-atom to which they are attached, together form a heterocyclic ring.

50 3. A process according to claim 1 conducted substantially as herein described with particular reference to the Examples and the dyeing example.

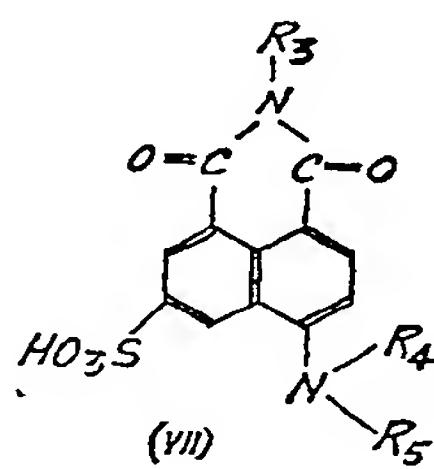
55 4. Materials dyed by a process according to any one of claims 1 to 3.

5. Naphthalimide compounds of the formula



5 wherein R and R₁, independently, each represents an optionally substituted hydrocarbon or heterocyclic radical, R₂ represents hydrogen or an optionally substituted hydrocarbon or heterocyclic radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R₁ and R₂, together with the N-atom to which they are attached, together form a heterocyclic ring, with the proviso that, when R₂ represents hydrogen, R and R₁ do not simultaneously represent an unsubstituted alkyl or aralkyl radical.

10 6. A compound according to claim 5 of the formula



20 wherein R₃ and R₄, independently, each represents an optionally substituted alkyl, aralkyl or cycloalkyl radical, and R₅ represents hydrogen or an optionally substituted alkyl, aralkyl or cycloalkyl radical or a reactive group capable of forming a covalent bond by reaction with a cellulosic or polyamide fibre, or R₄ and R₅, together with the N-atom to which they are attached, together form a heterocyclic ring, with the proviso that, when R₅ represents hydrogen, R₃ and R₄ do not simultaneously represent an unsubstituted alkyl or aralkyl radical.

25 7. A compound according to claim 6, wherein R₃ and R₄, independently, each represents an optionally substituted alkyl, aralkyl or cycloalkyl radical, and R₅ represents hydrogen or an optionally substituted alkyl, aralkyl or cycloalkyl radical, or R₄ and R₅, together with the N-atom to which they are attached, together form a heterocyclic ring, with the proviso that, when R₅ represents hydrogen, R₃ and R₄ do not simultaneously represent an unsubstituted alkyl or aralkyl radical.

30 8. A compound according to claim 7, wherein R₄ and R₅ together with the N-atom to which they are attached represent other than a heterocyclic ring.

35 9. A compound according to any one of claims 6 to 8, wherein R₅ represents hydrogen.

40 10. A compound according to any one of claims 6 to 9, wherein R₃ and R₄ each signify an optionally substituted cycloalkyl radical.

11. A compound according to any one of claims 6 to 10, wherein R₃ and R₄ are identical.

12. A compound according to any one of claims 6 to 11, wherein any alkyl radical is of 1 to 6 carbon atoms and any cycloalkyl radical is a cyclohexyl radical.

13. A compound according to claim 12, wherein any alkyl radical is of 1 to 4 carbon atoms.

14. A compound according to any one of claims 6 to 13, wherein any substituent on any alkyl radical is selected from hydroxy, halogen, cyano, sulphonic acid, alkoxy, acyl, amide, and amino radicals.

15. A compound according to claim 14, wherein any said substituent is hydroxy or sulphonic acid.

16. A compound according to any one of claims 6 to 13, wherein any alkyl radical is unsubstituted.

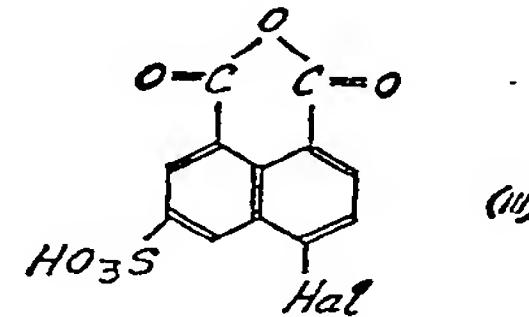
17. A compound according to any one of claims 6 to 16, wherein any cycloalkyl radical is unsubstituted or substituted by up to 3 methyl groups.

18. A compound according to any one of claims 5 to 17, in salt form.

19. A compound according to claim 18, in sodium salt, potassium salt, amine salt or ammonium salt form.

20. The particular naphthalimide compounds according to claim 5, herein described and exemplified.

21. A process for the production of a naphthalimide compound according to claim 5, which comprises reacting 1 mol of a compound of the formula

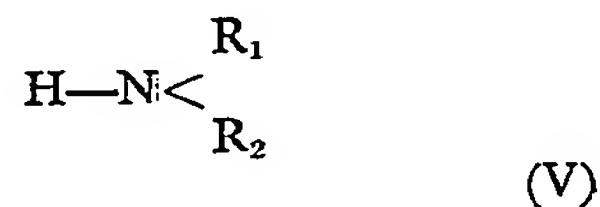


in which Hal represents a halogen atom, with 1 mol of an amine of the formula



(IV)

and 1 mol of an amine of the formula



where R, R₁ and R₂ have the meanings given in claim 5.

5 22. A process according to claim 21, which comprises reacting 1 mol of a compound of the formula (III) with 1 mol of a compound of the formula (V) and thereafter with 1 mol of a compound of the formula (IV).

10 23. A process according to claim 21 or claim 22 conducted substantially as herein described and exemplified.

24. Naphthalimide compounds according to claim 5 whenever prepared by a process according to any one of claims 21 to 23.

15 25. A dyeing process for a material comprising natural polyamide fibres which comprises applying to said material one or more compounds according to any one of claims 5 to 20 and 24.

20 26. Material comprising natural polyamide fibres dyed by a process according to claim 25.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70/72, Chancery Lane, London, WC2A 1AD,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.